

# UNIT 10

## PREPARATION OF AROMATIC HYDROCARBONS

### Structure

---

10.1	Introduction	10.7	Carcinogenic Nature of Benzene
	Expected Learning Outcomes		
10.2	Aromatic Hydrocarbons - An Introduction	10.8	Preparation of Benzene and Alkylbenzenes
	Huckel's Rule		Preparation of benzene
10.3	Occurrence		Preparation of Alkylbenzenes
10.4	Structure of Benzene	10.9	Summary
10.5	Physical Properties of Benzene	10.10	Terminal Questions
		10.11	Answers
10.6	Uses of Benzene and its Derivatives		

### 10.1 INTRODUCTION

---

Aromatic compounds are the backbone of organic chemistry. Many of the drugs contain aromatic compounds. So it is very important to understand the chemistry of aromatic compounds. Benzene is a basic aromatic hydrocarbon with general formula  $C_6H_6$ , having conjugated double bonds. Lots of household items like paints, varnish, detergents etc. contain aromatic compounds.

This is the first Unit of this block. In this unit first we will give you a brief introduction of aromatic compounds. Then we will discuss the isolation and occurrence of benzene. We will recall Huckel's rule for aromaticity. We will also learn the physical properties of benzene. In the last section of this unit, we will discuss different methods for the preparation of benzene and alkyl benzenes.

In the next two units we will familiarise you with the reactions of benzene and alkylbenzenes.

## Expected Learning Outcomes

After studying this unit you should be able to:

- ❖ explain the basic concept of aromatic hydrocarbons;
- ❖ explain Huckel's rule;
- ❖ describe the structure of benzene;
- ❖ describe the physical properties of benzene;
- ❖ describe the carcinogenic nature of benzene; and
- ❖ Outline the methods of preparation of benzene and alkylbenzene.

## 10.2 AROMATIC HYDROCARBONS – AN INTRODUCTION

You have already studied the basics of aromatic compounds in Unit 19 of 1<sup>st</sup> semester course. The word "benzene" derives from "gum benzoin" (benzoin resin), an aromatic resin. In the earlier stages, the organic compounds were arbitrarily classified as aliphatic or aromatic. The meaning of word "aliphatic" means fatty. The aliphatic compounds were so named because the fatty acids were one of the first members of this class. In addition to the aliphatic compounds, there was a large number of another type of compounds, which were also obtained from natural sources, e.g., resins, balsams, aromatic oils, etc. The structures of these compounds were as unknown but they had one thing in common, a pleasant odour. Thus, these compounds were arbitrarily classified as aromatic compounds (Greek: **aroma** 'fragrant smell'). There was a time when chemists used to smell the compound and sometimes even taste it to identify chemicals. Just because of this wrong practice, a famous Swedish Scientist **Carl Scheele** died while tasting a chemical substance in his laboratory. Another chemist "**Robert Bunsen**" used to taste poisonous arsenic and this made his tongue black.

In present scenario, word aromatic is used for benzene and its derivatives. Remember it does not mean that all the aromatic compounds contain benzene ring. There are number of aromatic compounds which do not contain benzene ring. These types of compounds are classified as **non-benzenoid** aromatic compounds. So we can say that aromatic compounds are of two types:

- i) **benzenoid** compounds; and
- ii) **non-benzenoid** compounds.

Before we proceed further, let us recall some important facts of aromatic compounds, which will help you to understand this unit. Benzene is a basic aromatic hydrocarbon with the chemical formula  $C_6H_6$ . Aromatic hydrocarbons

are compounds having alternate single and double bonds between the two carbon atoms of the ring.

A hydrocarbon can be an aromatic compound if it follows the Huckel's rule. Details of this rule you have studied in Unit 19 of the 1<sup>st</sup> Semester Course. Let us recall Huckel's rule.

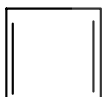
### 10.2.1 Huckle's Rule

According to Hückel's Rule, a compound can be aromatic if it contains the following distinct properties:

- The compound is a cyclic structure.
- The compound must contain  $(4n + 2) \pi$  electrons, where  $n$  is any number i.e. 1,2,3,4,..... This means that only the rings with 2, 6, 10, 14,..... $\pi$  electrons may be aromatic.
- The compound must be co- planar.

Some examples of the compounds following Huckel's rule are given below:

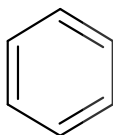
#### Cyclobutadiene



No. of  $\pi$ -electrons = 4

$4n + 2\pi$ -electrons are required for aromaticity. Cyclobutadiene has 4  $\pi$ -electrons, hence cyclobutadiene is not aromatic as it does not follow Huckel's rule.

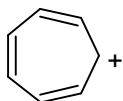
#### Benzene



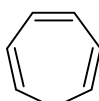
No. of  $\pi$ -electrons = 6

Benzene is a typical example of an aromatic compound. Here, the Huckel's rule is followed as it has 6 $\pi$  electrons which are required for a compound to be aromatic. All the carbon atoms of benzene ring are  $sp^2$  hybridised and it is a planar molecule. It is an excellent example of an aromatic system.

#### Cycloheptatrienyl cation and cycloheptatriene



1,3,5-cycloheptatrienyl cation



1,3,5-cycloheptatriene

In the above two compounds both have 6 $\pi$  electrons but 1, 3, 5-cycloheptatrienyl cation is aromatic and 1,3,5-cycloheptatriene is not. You

can ask why it is so. Cycloheptatriene has three double bonds i.e.  $6\pi$  electrons but because of the presence of one  $sp^3$  carbon atom it is not coplanar and hence not aromatic compound. In case of cycloheptatrienyl cation generation of the cation removes the hindrance and the delocalised  $6\pi$  electrons (Huckel's rule) make the cation planar and aromatic.

From the above example, it is clear that a flat planar geometry is required for proper overlap resulting in delocalisation of  $\pi$ -electrons which is a necessary condition for a compound to be aromatic.

---

### SAQ 1

1, 3, 5-cycloheptatrienyl cation is aromatic and 1,3,5-cycloheptatriene is not. Explain.

---

## 10.3 OCCURANCE

---

First time in 1825, Michael Faraday isolated benzene from whale oil giving it the name *bicarburet of hydrogen*. In 1833, a famous scientist Eilhard Mitscherlich obtained benzene by distilling benzoic acid and lime. He gave the compound the name *benzin*.

The biggest consumer country of benzene was China, followed by the USA. Benzene production is currently expanding in the Middle East and in Africa, whereas production capacities in Western Europe and North America are stagnating.

Benzene is produced naturally by volcanoes. In the year 1845, Holman isolated benzene and its derivatives from coal tar. Later on benzene became very important compound in organic chemistry as a large number of the medicines are aromatic in nature, e.g., aspirin, paracetamol, diclofinac sodium, etc.

Benzene is a natural constituent of crude oil and is one of the elementary petrochemicals. Benzene is a byproduct of the incomplete combustion of many materials. In earlier days benzene was obtained as a by-product of coke for the steel industry. After 1950s, the demand of benzene increased tremendously especially for the growing polymer industries, Today, major amount of benzene comes from the petrochemical industries, and only a small fraction is obtained from coal.

---

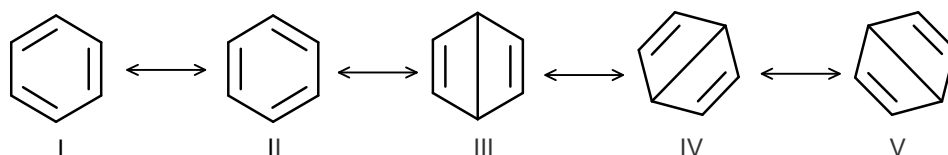
### SAQ 2

Fill in the following blanks

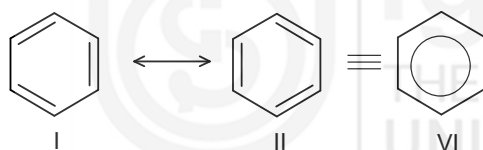
- In 1825, Michael Faraday isolated benzene from -----.
  - Benzin* was isolated from ----- and lime.
  - In 1845, Holman isolated benzene and its derivatives from -----.
  - is a byproduct of the incomplete combustion of many materials.
  - Today, major amount of benzene comes from -----.
-

## 10.4 STRUCTURE OF BENZENE

You have studied structure of benzene in Unit 19 of 1<sup>st</sup> semester course. Here we will just recall only important points which will help you to understand this unit. We cannot write a single structure for benzene which would encompass all its properties rather it is considered to be the resonance “hybrid” of the following hypothetical structures I-V:

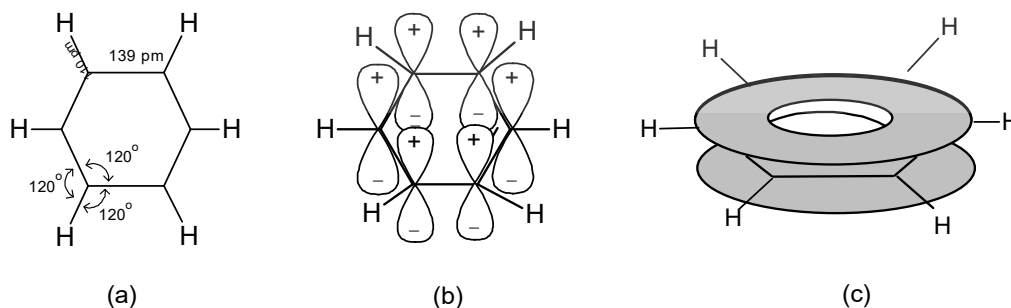


These structures are called resonance structures or contributors or canonical forms. The two “Kekule” forms, I and II, are of lower energy (more stable) than the three “Dewar” forms, III to V. Structures I and II could be expected to “contribute” more to the hybrid than either III, IV or V. Hence, the properties of benzene would be expected to resemble more closely to either I or II than to III, IV or V. Since I and II have the same energy, each would contribute to the hybrid by the same amount. The symbol of resonance, double-headed arrow ( $\longleftrightarrow$ ), does not indicate an equilibrium. The canonical structures I-V are hypothetical and do not have any physical existence. Structures I and II can be represented as structure VI. It shows that hydrogen atom is attached to each angle of benzene ring.



### Orbital picture of benzene

Benzene is visualised as a symmetrical, flat, planar molecule having a regular hexagonal shape. Each carbon atom is bonded to two other carbon atoms and one hydrogen atom by sigma bonds using  $sp^2$  hybrid orbitals, Fig. 10.1 (a). All the carbon-carbon bonds are of equal length of 139 pm, similarly all the carbon-hydrogen bond are of 110 pm. You will notice that all the bond angles of carbon-carbon and carbon-hydrogen atoms are equal i.e.  $120^\circ$ .



**Fig. 10.1: a)  $\sigma$  Skeleton of benzene; b)  $\pi$  Bond formation in benzene; c)  $\pi$  Cloud in benzene, aromatic sextet.**

The third  $p$  orbital of each carbon atom lies perpendicular to the plane of the molecule and has a lobe each, above and below the plane, as shown in Fig. 10.1 (b). These  $p$  orbitals have one electron each. The sideways overlap of

these  $p$  orbitals accounts for the  $\pi$  bonding in benzene. The six electrons which form an electron cloud above and below the plane of the ring are called aromatic sextet, Fig. 10.1 (c).

### SAQ 3

Draw the orbital picture of benzene.

**Octane number** is a measure of quality of gasoline: higher the octane number, better the fuel.

## 10.5 PHYSICAL PROPERTIES OF BENZENE

Aromatic Hydrocarbons are well known for their exceptional physical and chemical properties. In this section we will learn about some important physical properties of benzene.

Benzene is a colorless liquid at room temperature. It is highly flammable liquid which gives sooty yellow flame on heating. Benzene has sweet smell, which is responsible for the aroma around petrol stations. As benzene has a high octane number, it is an important component of gasoline.

Like other hydrocarbons, benzene is also non-polar in nature. Benzene is immiscible with water and miscible in organic solvents, such as acetone, aldehydes, ethers, carbon tetrachloride, chloroform and hexane etc. Benzene has been widely used as a solvent, but due to its carcinogenic nature it has been banned in most of the countries. Benzene is used to prepare azeotrope with water. Benzene is lighter than water and its density is  $0.87\text{ g cm}^{-3}$ . Boiling point of benzene is  $358.5\text{ K}$  ( $80.5\text{ }^{\circ}\text{C}$ ) and melting point is  $283.5\text{ K}$  ( $5.5\text{ }^{\circ}\text{C}$ ). Benzene evaporates into the air very quickly. Its vapors are heavier than air and may sink into low-lying areas.

## 10.6 USES OF BENZENE AND ITS DERIVATIVES

Because of the pleasant smell of benzene, in the 19th century benzene was used as an after-shave lotion but due to its carcinogenic nature it was replaced by methylbenzene, which has similar physical properties but it was not carcinogenic. You will be surprised to know that lot of household items contain benzene. Some of them are:

- Paint,
- lacquer,
- varnish removers,
- glues,
- furniture wax,
- detergents and
- thinners.

In several chemical industries, aromatic hydrocarbons have wide applications. Benzene is used mainly as an intermediate to make other chemicals like: ethylbenzene, cumene, cyclohexane, nitrobenzene, and alkylbenzenes. More than half of the entire benzene production is used for the preparation of

**Azeotrope** is a **mixture** of liquids that has a constant boiling. The boiling point of an **azeotropic mixture** may be higher or lower than that of any of its components.

ethylbenzene, a precursor to styrene, benzene is used to make plastics, resins, synthetic fibers, rubber lubricants, dyes, detergents, drugs and pesticides.

Due to carcinogenic nature of benzene, in most of the industries, it is being replaced by toluene as a substitute for benzene as a fuel additive.

---

### SAQ 4

Which of the following are true or false? Write “T” for true and “F” for false in the boxes given below

- i) Benzene is a colorless or light yellow liquid at room temperature. ☐
  - ii) Benzene has a low octane number. ☐
  - iii) Benzene is polar compound. ☐
  - iv) Benzene is immiscible with acetone. ☐
  - v) Benzene is used to prepare azeotrope with water. ☐
  - vi) Benzene is lighter than water. ☐
- 

## 10.7 CARCINOGENIC NATURE OF BENZENE

---

As benzene is a carcinogen, most non-industrial applications have been limited. Both International Agency for Research on Cancer (IARC) and Environmental Protection Agency (EPA) declared benzene as “carcinogenic compound”. It causes Acute Myeloid Leukemia (AML).

The major effect of benzene from long-term exposure is on the blood (Long-term exposure means exposure of a year or more). Benzene causes harmful effects on the bone marrow and can cause a decrease in red blood cells, leading to anemia. Benzene oxidises in the body to produce an epoxide, which itself is carcinogenic. The epoxide interacts with DNA to produce cancer.

Direct exposure of the eyes, skin, or lungs to benzene can cause tissue injury and irritation. Even death is possible if a person inhales very high levels of benzene. Inhalation of benzene may develop the following symptoms:

- Vomiting,
- Irritation of the stomach,
- Sleepiness,
- Drowsiness,
- Regular heartbeat.,
- Headaches,
- Tremors,
- Unconsciousness.

Benzene can react with other air pollutants to form ground levels ozone which can damage crops and other materials.

**IARC:** The International Agency for Research on Cancer is part of the World Health Organization (WHO). One of its goals is to identify causes of cancer.

**EPA:** Environmental Protection Agency is an agency of the United States federal government whose mission is to protect human and environmental health.

**AML: (Acute Myeloid Leukemia)** is a cancer of the blood and bone marrow. This type of cancer usually gets worse quickly if it is not treated.



## SAQ 5

What are the symptoms of benzene Inhalation?

## 10.8 PREPARATION OF BENZENE AND ALKYL BENZENES

Benzene and alkylbenzenes can be prepared by numerous methods. In this unit we will discuss only few of them.

### 10.8.1 Preparation of Benzene

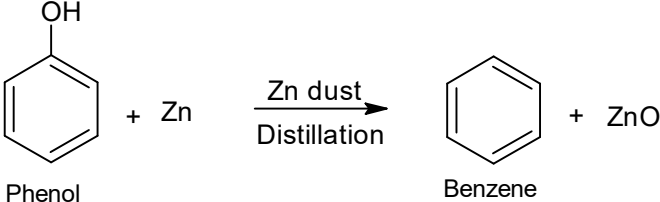
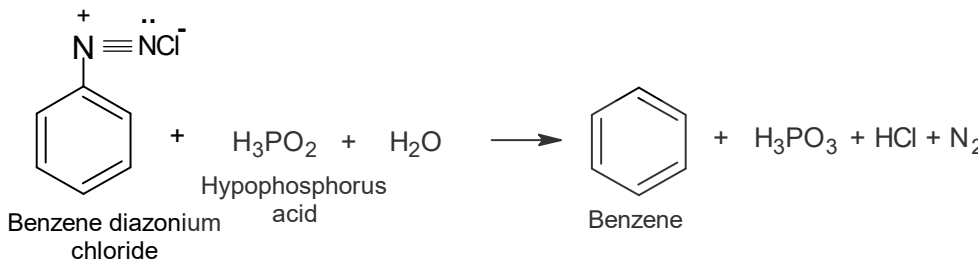
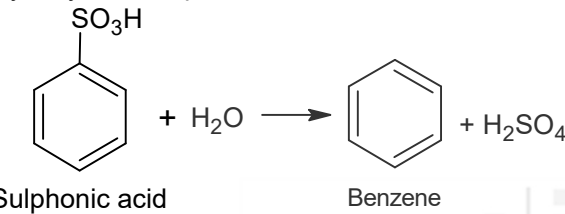
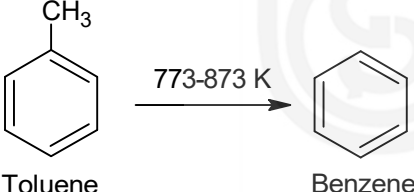
Benzene can be prepared from aromatisation of aliphatic hydrocarbons, cyclic polymerisation of ethyne, decarboxylation of sodium benzoate, reduction of phenol, hydrolysis of sulphonic acids and reduction of benzenediazonium salts.

Some important methods for preparation of benzene are summarised in Table 10.2.

Table 10.2: Methods of preparation benzene

Sr. No.	Reactions
1.	Aromatisation of aliphatic hydrocarbons
i)	$\text{CH}_3(\text{CH}_2)_4\text{CH}_3 \xrightarrow[\text{catalyst}]{\Delta} \text{Benzene}$ <p><i>n</i>-Hexane</p>
ii)	$\text{CH}_3(\text{CH}_2)_5\text{CH}_3 \xrightarrow[\text{catalyst}]{\Delta} \text{Toluene}$ <p><i>n</i>-Heptane</p>
iii)	$\text{CH}_3(\text{CH}_2)_6\text{CH}_3 \xrightarrow[\text{catalyst}]{\Delta} \text{Xylenes}$ <p><i>n</i>-Octane</p>
2.	<p>Cyclic polymerisation of ethyne</p> $3 \text{ HC}\equiv\text{CH} \xrightarrow[300^\circ\text{C}]{\text{Cu}} \text{Benzene}$ <p>Acetylene</p>
3.	<p>Decarboxylation of sodium benzoate</p> $\text{C}_6\text{H}_5\text{COONa} + \text{NaOH} \xrightarrow{\text{CaO}} \text{C}_6\text{H}_6 + \text{Na}_2\text{CO}_3$ <p>Sodium benzoate</p>

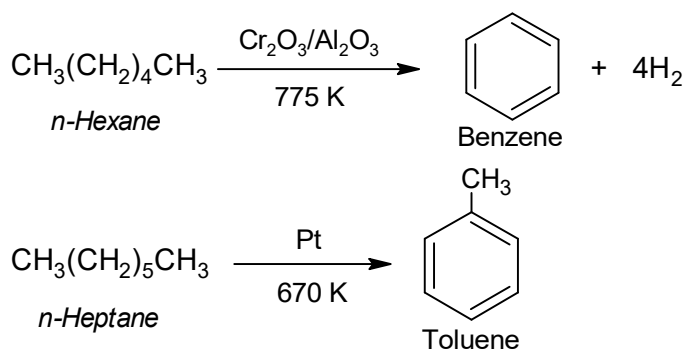


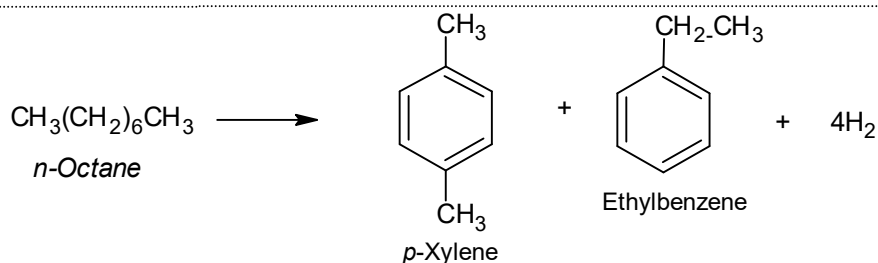
4.	<p>Reduction of phenol</p>  <p>Phenol + Zn <math>\xrightarrow[\text{Distillation}]{\text{Zn dust}}</math> Benzene + ZnO</p>
5.	<p>Reduction of Benzenediazonium Salts</p>  <p>Benzenediazonium chloride + H<sub>3</sub>PO<sub>2</sub> + H<sub>2</sub>O <math>\longrightarrow</math> Benzene + H<sub>3</sub>PO<sub>3</sub> + HCl + N<sub>2</sub></p>
6.	<p>Hydrolysis of sulphonic acids:</p>  <p>Sulphonic acid + H<sub>2</sub>O <math>\longrightarrow</math> Benzene + H<sub>2</sub>SO<sub>4</sub></p>
7.	<p>Hydrodealkylation</p>  <p>Toluene <math>\xrightarrow{773-873\text{ K}}</math> Benzene</p>

Let us study each method in detail.

### i) Aromatization of aliphatic hydrocarbons or Hydroforming

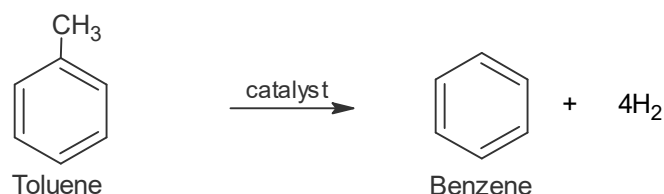
This is a process of converting aliphatic hydrocarbon to aromatic hydrocarbons. This is also known as **hydroforming or catalytic reforming**. Alkane with six or more carbon atoms, when heated strongly (775 K) under pressure in the presence of platinum catalyst, gives aromatic hydrocarbon. This process involves cyclisation, isomerisation and dehydrogenation. In this process, the product contains the same number of carbon atoms as the aliphatic starting materials. Aromatization of gasoline increases their octane number from 40 to 95 because unsaturated hydrocarbons are better fuels.





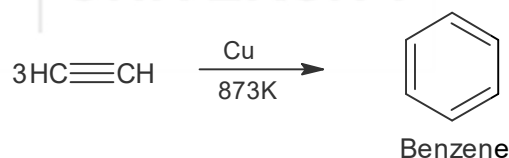
Catalytic aromatisation in the presence of platinum is sometimes referred to as platforming or hydroforming. This process also constitutes a valuable method for commercial production of these hydrocarbons.

Since, benzene is obtained in much smaller amount than toluene can be converted into benzene by heating with hydrogen under pressure in the presence of a metal oxide catalyst. This process is called **hydro-dealkylation**.

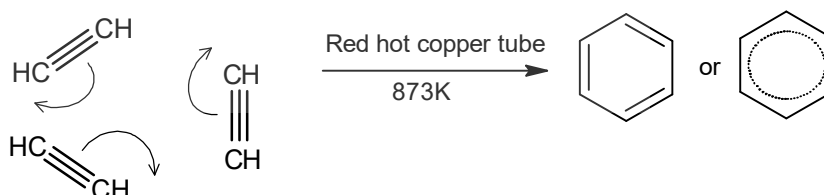


## ii) Cyclic Polymerisation of Ethyne

Ethyne undergo two types of polymerisation reaction- i) linear and ii) cyclic. Cyclic polymerization of ethyne results in the formation of aromatic hydrocarbons. It is one of the important chemical reactions of alkynes. When ethyne (acetylene) gas is passed through a red hot copper tube at 873 K, the ethyne molecules then undergo cyclic polymerization to form benzene.

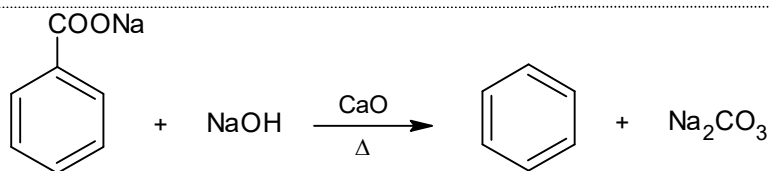


Here copper acts as catalyst. Three molecules of ethyne are involved in this reaction. This can be explained from following mechanism.



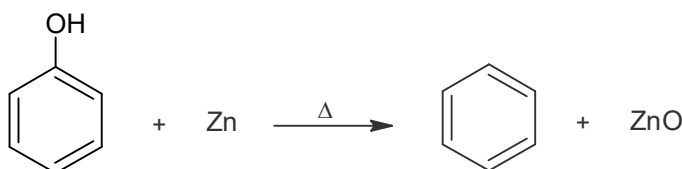
## iii) Decarboxylation of sodium benzoate

Benzene can be prepared from aromatic acids. Decarboxylation of sodium benzoate gives benzene. Reaction of sodium salt of the benzoic acid (sodium benzoate) with sodium hydroxide in presence of calcium hydroxide (mixture of sodium hydroxide and calcium hydroxide is known as soda lime) gives benzene and sodium carbonate. This is a common method of preparation of benzene in laboratory. For example:



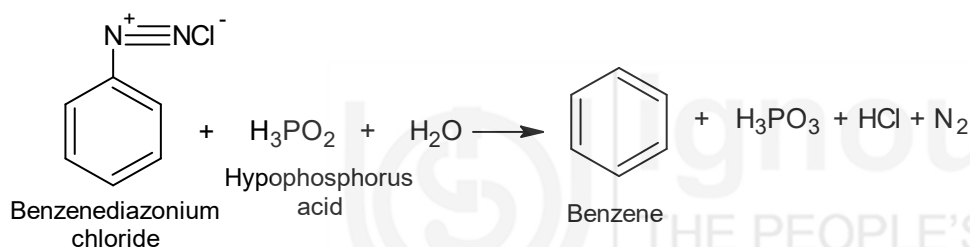
#### iv) Reduction of phenol

Benzene can be prepared by reduction of phenol. When phenol vapours are passed over heated zinc dust, benzene is formed. This reaction takes place in presence of strong reducing agents like zinc with strong heating.



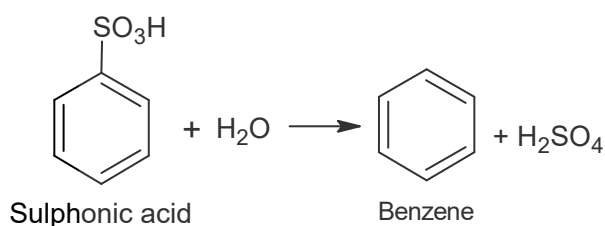
#### v) Reduction of Benzenediazonium Salts

Benzene can be prepared from benzenediazonium salts by heating it. Reduction of benzenediazonium chloride with hypophosphorus acid yields benzene.



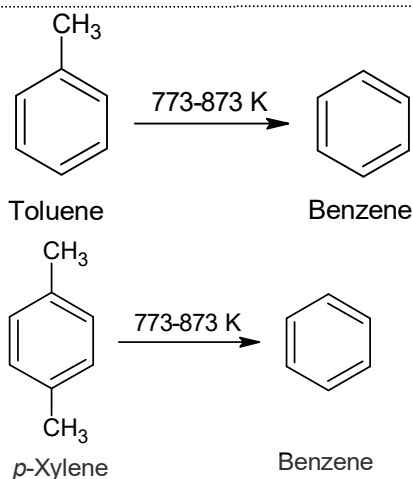
#### vi) Hydrolysis of sulphonic acid

Benzene can be prepared by hydrolysis of sulphonic acids. In this reaction, sulphonic acid is exposed to superheated steam leading to the formation of benzene.



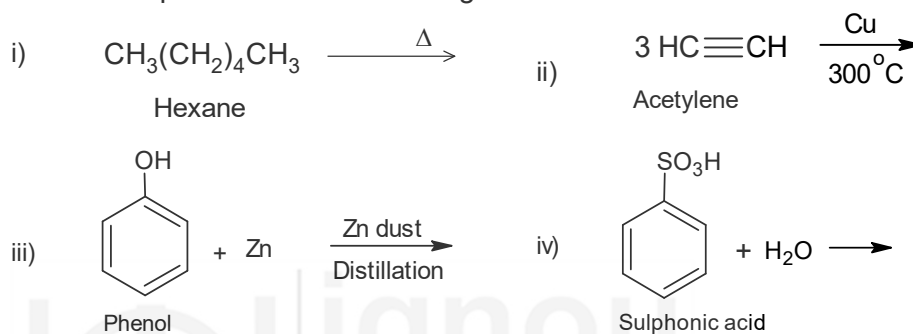
#### vii) Hydrodealkylation of Toluene

Toluene can be converted into benzene by dealkylation. In this reaction toluene and hydrogen is heated at a high temperature (773-873 K) and 40–60 atm pressure, in presence of a catalyst chromium, molybdenum, or platinum oxide. Sometimes, much higher temperatures are used instead of a catalyst (at the similar reaction condition). Under these conditions, toluene undergoes dealkylation to benzene and methane. This reaction gives good yield benzene i.e. about 95. Xylenes can also be converted into benzene with similar efficiency.



### SAQ 6

Predict the products of the following reactions:

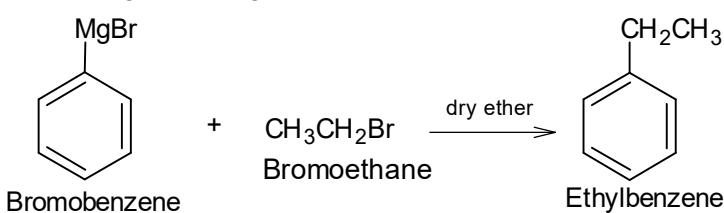
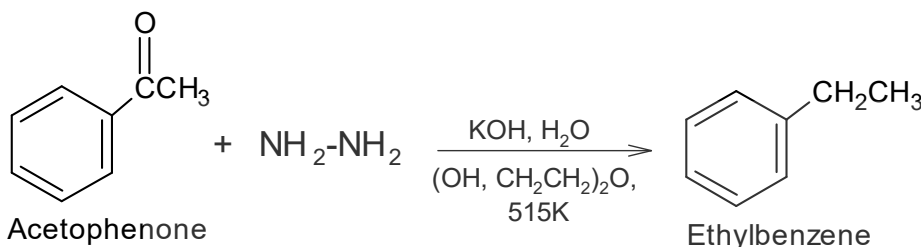
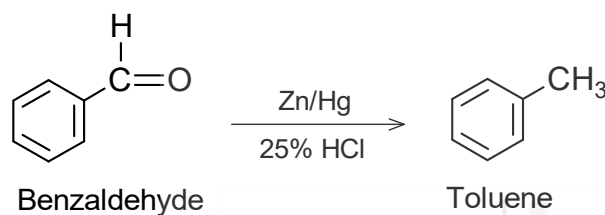


### 10.8.2 Preparation of Alkylbenzenes

Alkylbenzenes are very important aromatic compounds. They can be prepared from Friedel-Crafts alkylation, Wurtz-Fittig reaction, Grignard reagent, Wolff-Kishner reduction and Clemmensen reduction. Some important methods for preparation of alkylbenzenes are summarised in Table 10.3.

**Table 10.3: Methods of preparation alkylbenzenes (Arenes)**

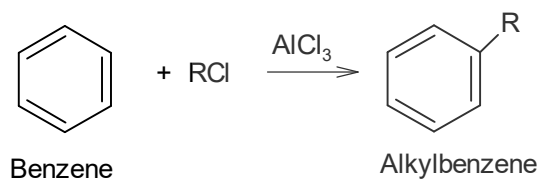
Sr. No.	Reactions
1.	Friedel-Crafts Alkylation  Benzene $\xrightarrow{\text{CH}_3\text{CH}_2\text{Cl} \cdots \cdots \text{AlCl}_3}$ Ethylbenzene
2.	Wurtz-Fittig reaction  Bromobenzene + 2Na + CH <sub>3</sub> CH <sub>2</sub> Br $\xrightarrow{\text{dry ether}}$ Ethylbenzene + 2NaBr

3.	<p>From Grignard reagent</p>  <p>Bromobenzene + <math>\text{CH}_3\text{CH}_2\text{Br}</math> (Bromoethane) <math>\xrightarrow{\text{dry ether}}</math> Ethylbenzene</p>
4.	<p>Wolff-Kishner reduction</p>  <p>Acetophenone + <math>\text{NH}_2\text{-NH}_2</math> <math>\xrightarrow[\text{515K}]{\text{KOH, H}_2\text{O}, (\text{OH, CH}_2\text{CH}_2)_2\text{O}}</math> Ethylbenzene</p>
5.	<p>Clemmensen Reduction</p>  <p>Benzaldehyde <math>\xrightarrow[25\% \text{ HCl}]{\text{Zn/Hg}}</math> Toluene</p>

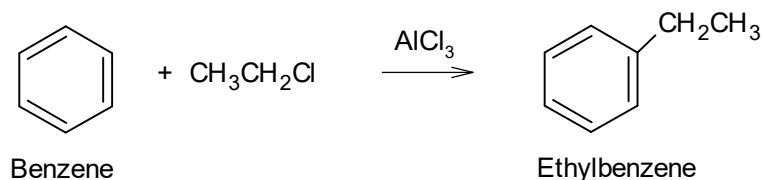
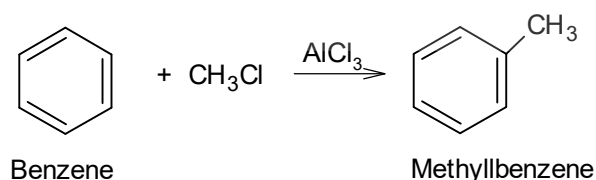
Now let us discuss each reaction in detail.

### i) Friedel-Crafts Alkylation

Benzene on heating with a haloalkane in the presence of anhydrous aluminum chloride gives its homologue, alkylbenzene. This reaction is known as **Friedel-Crafts reaction**. Details of this reaction you will learn in Unit 11 of this course.



Benzene on heating with chloromethane gives methylbenzene (toluene) and with chloroethane it gives ethylbenzene.



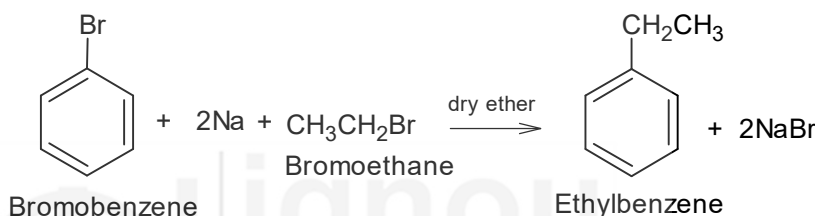
**ii) Wurtz–Fittig reaction:**

In year 1855, Charles-Adolphe Wurtz reported a reaction what is now known as the Wurtz reaction. In Wurtz reaction, two molecules of alkyl halide are treated with sodium in dry ether to give alkanes. Details of this reaction, you have studied in Unit 15 of 1<sup>st</sup> semester course

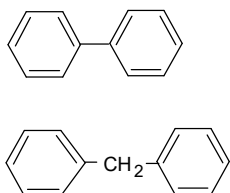


In the 1860s, another scientist Rudolph Fittig extended the Wurtz reaction by coupling of an alkyl halide with an aryl halide. This modification of the Wurtz reaction is considered a separate process and is named for both scientists i.e. **Wurtz–Fittig reaction**.

Alkylbenzenes, also known as Arenes, can be obtained by the reaction aryl halides and alkyl halide. In this reaction aryl halides and alkyl halides are treated with sodium in presence of dry ether. The result is the joining of alkyl and phenyl groups with the loss of halogens. The product is alkyl benzene (Arenes). This reaction is called **Wurtz–Fittig reaction**



**Biphenyl:** In isolated systems, two or more rings are joined to each other either directly or through carbon chain.



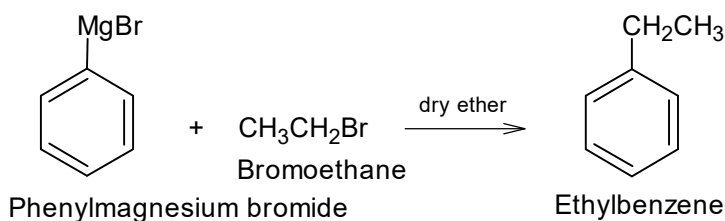
The Wurtz-Fittig reaction can also take place with metals other than sodium, like potassium, iron, copper, and lithium. In presence of lithium, it gives good yield but under ultrasonic irradiation.

The reaction works best for forming asymmetrical products. Typically the reaction is used for the alkylation of aryl halides. However, with the use of ultrasound, the reaction can also be made useful for the production of biphenyl compounds

Like Wurtz reaction, Wurtz-Fittig reaction also gives some undesired side products, which limits its applications.

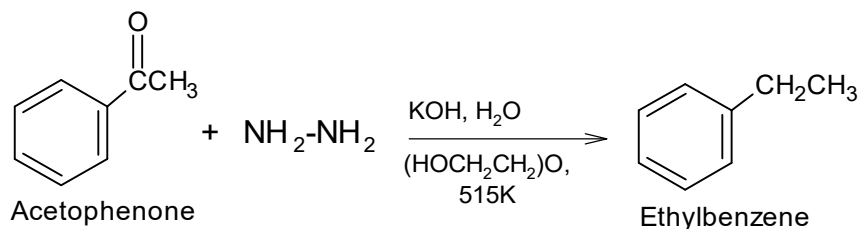
**iii) From Grignard Reagent:**

Alkylbenzenes (Arenes) can also be prepared by the reaction of arylmagnesium halide (Grignard reagent) and alkylhalide. For example

**iv) Wolff-Kishner Reduction**

Aldehydes and ketones can be reduced to alkanes by treating them with hydrazine, H<sub>2</sub>N – NH<sub>2</sub>, at a high temperature, in alkaline medium. This reaction

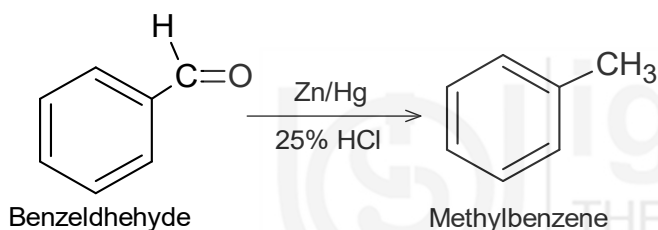
is known as Wolff-Kishner reduction. It is a useful synthetic method for converting an aldehyde or a ketone to an alkane. For example,



Wolff-Kishner reduction can be carried out at room temperature if a strong base like potassium 2-methyl-2-propoxide is used in a polar solvent like dimethyl sulphoxide

#### v) Clemmensen Reduction

Clemmensen Reduction is used to reduce alkylhalide and ketones this results in the conversion of CO group to CH<sub>2</sub> group. In other words aldehydes and ketones can be converted to the corresponding alkanes under acidic conditions by **Clemmensen reduction**. In this reaction, zinc amalgam (an alloy of zinc and mercury) and concentrated HCl are used to reduce an aldehyde or ketone.



Wolff-Kishner or Clemmensen reduction is particularly useful for the synthesis of compounds having alkyl groups attached to benzene ring. You may recall that Friedel-Crafts alkylation can also be used for this purpose. But in Friedel-Crafts alkylation, rearrangement of the alkyl groups is usually observed.

## 10.9 SUMMARY

- Benzene is a basic aromatic hydrocarbon with the chemical formula C<sub>6</sub>H<sub>6</sub>. Aromatic Hydrocarbons are compounds having alternate  $\sigma$  and  $\pi$  bonds between the carbon atoms of the ring.
- A hydrocarbon can be an aromatic compound if it follows the Huckel's Rule and is a planar molecule. According to Huckel's Rule, a compound must contain  $(4n + 2)$   $\pi$  electrons, (where  $n$  is any number i.e., 0,1,2,3,4.....) and must be co-planar.
- Benzene is produced naturally by volcanoes. Coal tar is a good source of benzene.
- Benzene is a colorless highly flammable liquid at room temperature.
- Benzene is non-polar solvent which is immiscible with water and miscible in organic solvents. Benzene is lighter than water and its density is 0.87g



$\text{cm}^{-3}$ . Boiling point of benzene is 358.5 K (80.5 °C) and melting is 283.5 K (5.5 °C)

- Lot of household items like paint, lacquer, varnish removers, glues, furniture wax, detergents and thinners contain benzene.
- Benzene can be prepared by:
  - Aromatization of aliphatic hydrocarbons or hydroforming
  - Cyclic Polymerization of ethyne
  - Decarboxylation of sodium benzoate
  - Reduction of phenol
  - Reduction of benzenediazonium Salts
  - Hydrolysis of sulphonic acids
  - Dealkylation of toluene
- Alkylbenzene can be prepared by:
  - Friedel-Crafts alkylation
  - Wurtz–Fittig reaction
  - Grignard reagent
  - Wolff-Kishner reduction
  - Clemmensen reduction

## 10.10 TERMINAL QUESTIONS

---

1. What are the main points of Huckel's rule?
2. How would you prepare benzene from ethyne? Give its mechanism
3. What is hydroforming? Explain with the help of an example.
4. Give one example of the following name reactions
  - i) Friedel-Crafts Alkylation
  - ii) Wurtz-Fittig reaction
  - iii) Clemmensen Reduction
  - iv) Wolff-Kishner reduction

## 10.11 ANSWERS

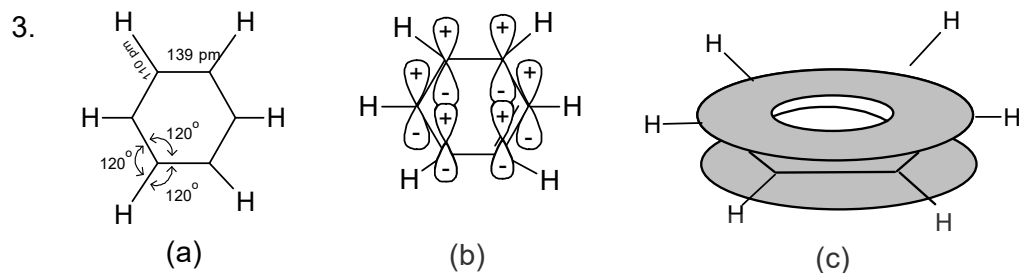
---

### Self-Assessment Questions

---

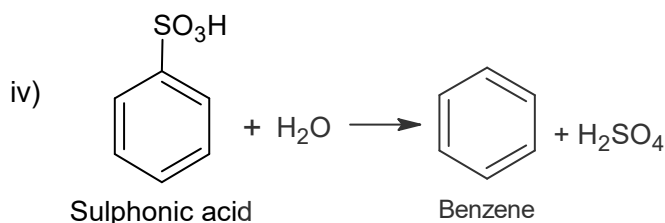
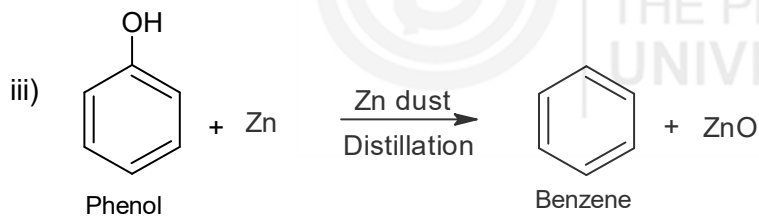
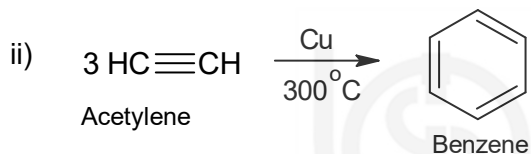
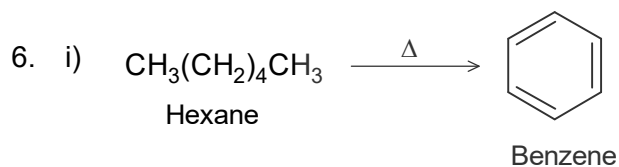
1. Cycloheptatriene has three double bonds i.e.  $6\pi$  electrons but because of the presence of one  $sp^3$  carbon atom it is not coplanar and hence not aromatic compound. In case of cycloheptatrienyl cation, generation of the cation removes the hindrance and the delocalised  $6\pi$  electrons (Huckel rule) make the cation planar and aromatic.

2. i) whale oil  
 ii) benzoic acid  
 iii) coal tar.  
 iv) benzene  
 v) the petrochemical industries.



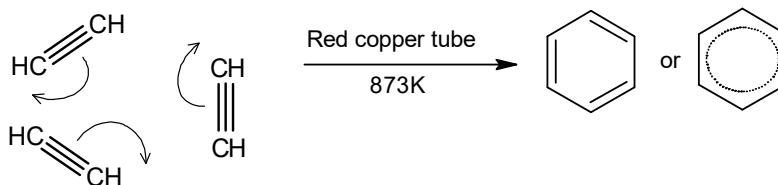
4. i) T, ii) F, iii) F, iv) F, v) T, vi) T

5. Vomiting, irritation of the stomach, sleepiness, drowsiness, irregular heartbeat, headaches, tremors, unconsciousness.

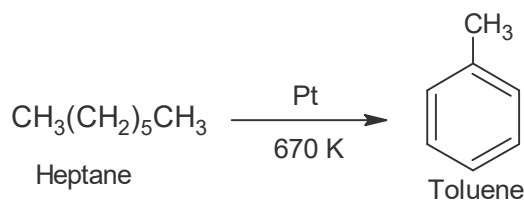
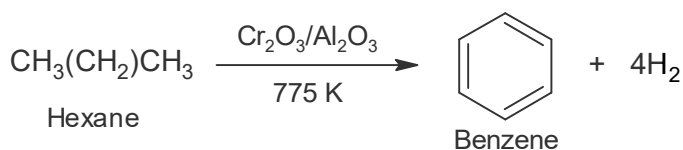


## Terminal Questions

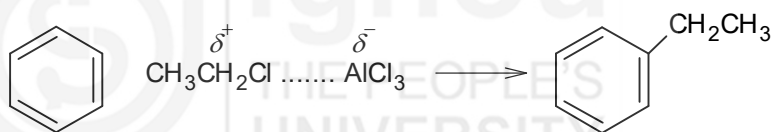
- The important points of Hückel's rule are:
  - The compound should be a cyclic structure.
  - The compound must contain  $(4n + 2)$   $\pi$  electrons, where  $n$  is any number i.e. 0,1,2,3,4..... This means that only the ring with 2, 6, 10, 14,..... $\pi$  electrons may be aromatic.
  - The compound must be co-planar.
- Cyclic polymerisation of ethyne results in the formation of aromatic hydrocarbons. When ethyne (acetylene) gases is passed through a red hot copper tube at 873 K, The ethyne molecules then undergo cyclic polymerization to form benzene.



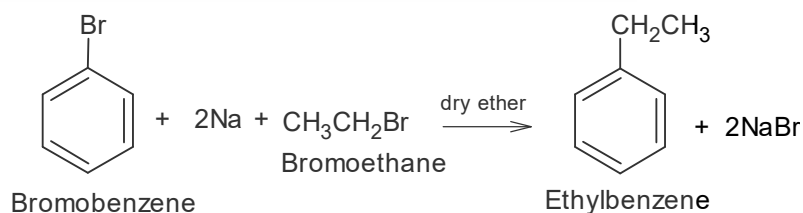
3. This is a process of converting aliphatic hydrocarbon to aromatic hydrocarbons. This is also known as **hydroforming or catalytic reforming**. Alkane with six or more carbon atoms, when heated strongly (775 K) under pressure in the presence of platinum catalyst, gives aromatic hydrocarbon. This process involves cyclisation, isomerisation and dehydrogenation. In this process the product contains the same number of carbon atoms as the aliphatic starting materials.



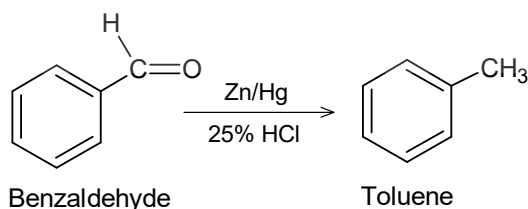
4. i) Friedel-Crafts Alkylation



- ii) Wurtz-Fittig reaction



- iii) Clemmensen Reduction



- iv) Wolff-Kishner reduction

